CLAIMS:

1. A method of making a carboxylated carbohydrate product which comprises:

oxidizing a carbohydrate compound by reacting it in an aqueous system with a sufficient amount of a primary oxidant selected from the group consisting of hindered heterocyclic oxammonium salts in which the carbon atoms adjacent the oxammonium nitrogen lack α-hydrogen substitution, the corresponding amines, hydroxylamines, and nitroxides of these oxammonium salts, and mixtures thereof, and a secondary oxidant selected from chlorine dioxide and latent sources of chlorine dioxide in a sufficient amount to induce an increase in carboxyl substitution in the carbohydrate of at least 2 meq/100g.

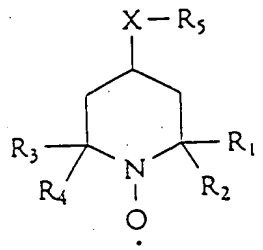
2. The method of claim 1 in which the carbohydrate is selected from the group consisting of cellulose and starch.

3. The method of claim 2 in which the carbohydrate product is a starch.

4. The method of claim 2 in which the carbohydrate product is cellulose.

5. The method of claim 1 in which the nitroxides have a five or six membered ring structure with di-lower alkyl substitution on each carbon atom adjacent the nitroxide.

6. The method of claim 5 in which the nitroxides are compositions having the structure



in which R_1-R_4 are one to four carbon alkyl groups but R_1 with R_2 and R_3 with R_4 may together be included in a five or six carbon alicyclic ring structure, X is sulfur or oxygen, and R_5 is hydrogen, C_1-C_{12} alkyl, benzyl, 2-dioxanyl, a dialkyl ether, an alkyl

polyether, or a hydroxyalkyl, and X with R_5 being absent may be hydrogen or a mirror image moiety to form a bipiperidinyl nitroxide.

7. The method of claim 6 in which the nitroxide is 2,2,6,6-tetramethylpiperidinyl-1-oxy free radical.

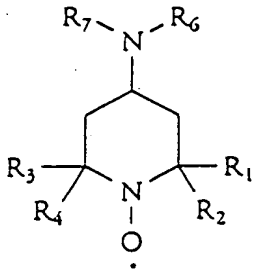
8. The method of claim 6 in which the nitroxide is 2,2,2′,2′,6,6,6′,6′octamethyl-4,4′-bipiperidinyl-1,1′-dioxy di-radical.

9. The method of claim 6 in which the nitroxide is 2,2,6,6-tetramethyl-4-hydroxypiperidinyl-1-oxy free radical.

10. The method of claim 6 in which the nitroxide is 2,2,6,6-tetramethyl-4-methoxypiperidinyl-1-oxy free radical.

11. The method of claim 6 in which the nitroxide is 2,2,6,6-tetramethyl-4- benzyloxypiperidinyl-1-oxy free radical.

12. The method of claim 5 in which the nitroxides are compositions having the structure

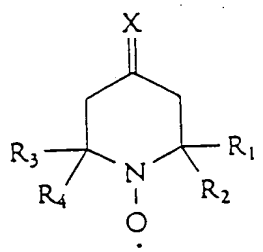


in which R_1-R_4 are one to four carbon alkyl groups but R_1 with R_2 and R_3 with R_4 may together be included in a five or six carbon alicyclic ring structure, and R_6 is hydrogen or C_1- C_5 alkyl, and R_7 is hydrogen, C_1-C_8 alkyl, phenyl, carbamoyl, alkyl carbamoyl, phenyl carbamoyl, or C_1-C_8 acyl.

13. The method of claim 12 in which the nitroxide is 2,2,6,6-tetramethyl-4-aminopiperidinyl-1-oxy free radical.

14. The method of claim 12 in which the nitroxide is 2,2,6,6-tetramethyl-4-acetylaminopiperidinyl-1-oxy free radical.

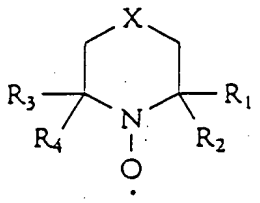
15. The method of claim 5 in which the nitroxides are compositions having the structure



In which R_1-R_4 are one to four carbon alkyl groups but R_1 with R_2 and R_3 with R_4 may together be included in a five or six carbon alicyclic ring structure, and X is oxygen, sulfur, NH, N-alkyl, NOH, or NOR_8 where R_8 is lower alkyl.

16. The method of claim 15 in which the nitroxide is 2,2,6,6-tetramethyl-4-piperidone-1-oxy free radical.

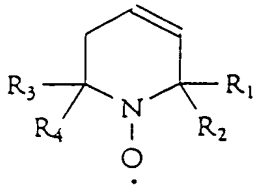
17. The method of claim 5 in which the nitroxides are compositions having the structure



wherein R_1-R_4 are one to four carbon alkyl groups but R_1 with R_2 and R_3 with R_4 may be linked into a five or six carbon alicyclic ring structure, X is oxygen, sulfur, -alkyl amino, or acyl amino.

18. The method of claim 17 in which the nitroxide is 3,3,5,5-tetramethylmorpholine-1-oxy free radical.

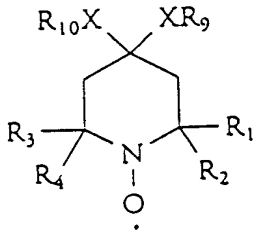
19. The method of claim 5 in which the nitroxides are compositions having the structure



wherein R_1-R_4 are one to four carbon alkyl groups but R_1 with R_2 and R_3 with R_4 may be linked into a five or six carbon alicyclic ring structure.

20. The method of claim 19 in which the nitroxide is 3,4-dehydro-2,2,6,6,-tetramethylpiperidinyl-1-oxy free radical.

21. The method of claim 5 in which the nitroxides are compositions having the structure



wherein R_1-R_4 are one to four carbon alkyl groups but R_1 with R_2 and R_3 with R_4 may together be included in a five or six carbon alicyclic ring structure, X is methylene, oxygen, sulfur, or alkylamino, and R_9 and R_{10} are one to five carbon alkyl groups and may together be included in a five or six member ring structure which, in turn, may have one to four lower alkyl or hydroxy alkyl substituents.

22. The method of claim 21 in which each X is oxygen, the oxygen atoms being linked by a two to three carbon alkyl chain to form a cyclic ketal substituent.

23. The method of claim 22 in which the nitroxide composition is the 1,2-ethanediol cyclic ketal of 2, 2, 6, 6-tetramethyl-4-piperidone-1-oxy free radical.

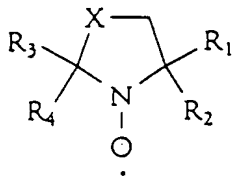
24. The method of claim 22 in which the nitroxide composition is the 1,3-propanediol cyclic ketal of 2,2,6,6-tetramethyl-4-piperidone-1-oxy free radical.

25. The method of claim 22 in which the nitroxide composition is the 2,2-dimethyl-1,3-propanediol cyclic ketal of 2,2,6,6-tetramethyl-4-piperidone-1-oxy free radical.

26. The method of claim 22 in which the nitroxide is the glyceryl cyclic ketal of 2,2,6,6-tetramethyl-4-piperidone-1-oxy free radical.

27. The method of claim 5 in which the nitroxides have a five atom ring structure with 2,2,5,5 lower alkyl substitution.

28. The method of claim 27 in which the nitroxides are compositions having the structure



in which R_1-R_4 are one to four carbon alkyl groups but R_1 with R_2 and R_3 with R_4 may together be included in a five or six carbon alicyclic ring structure, and X may be methylene, sulfur, oxygen, -NH, or NR_{11}, in which R_{11} is a lower alkyl.

29. The method of claim 28 in which the nitroxide composition is 2,2,5,5-tetramethylpyrrolidinyl-1-oxy free radical.

30. The method of claim 1 in which the aqueous system is buffered to a pH between about 4-12 during the oxidizing reaction.

31. The method of claim 30 in which the aqueous system is buffered to a pH between about 6-8 during the oxidizing reaction.

32. The method of claim 1 in which the primary oxidant is present in a range of 0.005-1.0% based on weight of carbohydrate present.

33. The method of claim 32 in which the primary oxidant is present in the range of 0.02-0.25% based on weight of carbohydrate present.

34. The method of claim 1 in which the secondary oxidant is present in the range of 0.2-35% based on weight of carbohydrate present.

35. The method of claim 34 in which the secondary oxidant is present in the range of 0.5-10 % based on weight of carbohydrate present.

36. The method of claim 1 in which the initial oxidation step is carried out for a time between 0.5 minutes and about 50 hours.

37. The method of claim 36 in which the initial oxidation step is carried out for a time between about 10 minutes to 2 hours.

38. The method of claim 1 in which the carbohydrate is a polymeric compound and which further comprises protecting the carbohydrate against degree of polymerization (D.P.) loss by further treating it in aqueous suspension with a stabilizing agent selected from the group consisting of oxidizing agents and reducing agents in order to remove any substituents which tend to cause molecular chain breakage.

39. The method of claim 38 in which the carbohydrate compound is cellulose.

40. The method of claim 39 which further comprises treating the carboxylated cellulose fibers with a tertiary oxidizing agent to stabilize the product by substantially converting any aldehyde substituents to additional carboxyl groups.

41. The method of claim 40 which comprises further stabilizing the carboxylated cellulose fibers after treatment with the tertiary oxidizing agent by treatment with a reducing agent.

42. The method of claim 40 in which the tertiary oxidant is selected from the group consisting of alkali metal chlorites, a chlorine dioxide/hydrogen peroxide mixture, and peracids.

43. The method of claim 42 in which the tertiary oxidant is a mixture of chlorine dioxide and hydrogen peroxide.

44. The method of claim 43 in which the chlorine dioxide is present in an amount of about 0.01-20% based on the weight of cellulose and the hydrogen peroxide is present in an amount of about 0.01-10% by weight of cellulose.

45. The method of claim 44 in which the chlorine dioxide is present in an amount of about 0.3-1.0% based on the weight of cellulose and the hydrogen peroxide is present in an amount of about 0.05-1.0% by weight of cellulose.

46. The method of claim 42 in which the tertiary oxidant is sodium chlorite.

47. The method of claim 46 in which the sodium chlorite is present during the stabilization reaction in a concentration of 0.1-20% by weight of cellulose.

48. The method of claim 47 in which the sodium chlorite is present during the stabilization reaction in a concentration of 1-9% by weight of cellulose.

49. The method of claim 42 in which the tertiary oxidant is a peracid.

50. The method of claim 40 in which the tertiary oxidant is present in the aqueous suspension during the stabilization reaction in a molar ratio of 1.5 – 15 times the aldehyde substitution on the carboxylated cellulose.

51. The method of claim 50 in which the tertiary oxidant is present in the aqueous suspension during the stabilization reaction in a molar ratio of 5 – 10 times the aldehyde substitution on the carboxylated cellulose.

52. The method of claim 40 in which the oxidation during the stabilization reaction proceeds for a time between 5 minutes and 50 hours.

53. The method of claim 52 in which the oxidation during the stabilization reaction proceeds for a time between 10 minutes and 2 hours.

54. The method of claim 41 in which the tertiary oxidizing agent is sodium chlorite and the reducing agent is sodium borohydride.

55. The method of claim 40 in which the oxidative stabilization treatment is carried out under acidic conditions at a pH between about 0-5.

56. The method of claim 55 in which the oxidative stabilization treatment is carried out under acidic conditions at a pH between about 2-4.

57. The method of claim 39 which further comprises treating the carboxylated cellulose fibers with a reducing agent to stabilize the product by substantially converting any aldehyde or ketone carbonyl substituents to hydroxyl groups.

58. The method of claim 57 in which the reducing agent in the aqueous suspension is a borohydride salt selected from the group consisting of alkali metal borohydrides, cyanoborohydrides, and mixtures thereof.

59. The method of claim 58 in which the reducing agent is present in an amount of about 0.1-4% by weight of oxidized cellulose

60. The method of claim 58 in which the reducing agent is present in an amount of about 1-3% by weight of oxidized cellulose present.

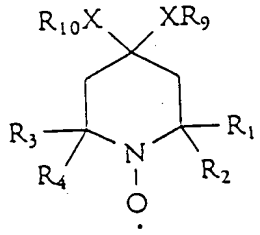
61. The method of claim 58 in which the reduction reaction proceeds for a time between 10 minutes and 2 hours.

62. The method of claim 4 in which the cellulose is fibrous and is selected from the group consisting of bleached and unbleached kraft wood pulps, prehydrolyzed kraft wood pulps, sulfite wood pulps and mixtures thereof.

63. The method of claim 62 in which the cellulose fiber is recycled secondary fiber.

64. A method of making a carboxylated carbohydrate product which comprises:

oxidizing a carbohydrate compound by reacting it in an aqueous system with a sufficient amount of a primary oxidant selected from the group consisting of hindered cyclic nitroxides having the composition



wherein R_1-R_4 are one to four carbon alkyl groups but R_1 with R_2 and R_3 with R_4 may together be included in a five or six carbon alicyclic ring structure, X is methylene, oxygen, sulfur, or alkylamino, and R_9 and R_{10} are one to five carbon alkyl groups and may together be included in a five or six member ring structure which, in turn, may have one to four lower alkyl or hydroxy alkyl substituents; and

a secondary oxidant selected from chlorine dioxide and latent sources of chlorine dioxide in a sufficient amount to induce an increase in carboxyl substitution in the carbohydrate of at least 2 meq/100g.

65. The method of claim 64 in which each X is oxygen, the oxygen atoms being linked by a two to three carbon alkyl chain to form a cyclic ketal substituent.

66. The method of claim 65 in which the cyclic ketal is selected from the group consisting of the 1,2-ethanediol, 1,3-propanediol, 2,2-dimethyl-1,3-propanediol, and glyceryl ketals of 2,2,6,6-tetramethyl-4-piperidone-1-oxy free radicals and mixtures thereof.

67. The method of claim 66 in which the nitroxide composition is the 1,2-ethanediol cyclic ketal of 2, 2, 6, 6-tetramethyl-4-piperidone-1-oxy free radical.

68. The method of claim 66 in which the nitroxide composition is the 1,3-propanediol cyclic ketal of 2,2,6,6-tetramethyl-4-piperidone-1-oxy free radical.

69. The method of claim 66 in which the nitroxide composition is the 2,2-dimethyl-1,3-propanediol cyclic ketal of 2,2,6,6-tetramethyl-4-piperidone-1-oxy free radical.

70. The method of claim 65 in which the nitroxide is the glyceryl cyclic ketal of 2,2,6,6-tetramethyl-4-piperidone-1-oxy free radical.

71. The method of claim 64 in which the carbohydrate is a polymeric compound and which further comprises protecting the carbohydrate against degree of polymerization (D.P.) loss by further treating it in aqueous suspension with a stabilizing agent selected from the group consisting of oxidizing agents and reducing agents in order to remove any substituents which tend to cause molecular chain breakage.

72. The method of claim 71 in which the carbohydrate compound is cellulose.

73. The method of claim 72 which further comprises treating the carboxylated cellulose fibers with a tertiary oxidizing agent to stabilize the product by substantially converting any aldehyde substituents to additional carboxyl groups.

74. The method of claim 73 in which the tertiary oxidant is selected from the group consisting of alkali metal chlorites, a chlorine dioxide/hydrogen peroxide mixture, and peracids.

75. The method of claim 74 in which the tertiary oxidant is a mixture of chlorine dioxide and hydrogen peroxide.

76. The method of claim 74 in which the tertiary oxidant is sodium chlorite.

77. The method of claim 74 in which the tertiary oxidant is a peracid.

78. The method of claim 72 in which the cellulose is fibrous and is selected from the group consisting of bleached and unbleached kraft wood pulps, prehydrolyzed kraft wood pulps, sulfite wood pulps and mixtures thereof.

79. The method of claim 78 in which the cellulose fiber is recycled secondary fiber.